REACTION OF DIPHENYL AMIDOPHOSPHATE WITH PHOSPHORUS PENTACHLORIDE

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UDC 542.91:547.1'118

Previously [1] it was reported that diphenyl amidophosphate reacts with PCl_5 to give (diphenoxyphosphorylimido)trichlorophosphate (I):

$$(PhO)_2P(O)NH_2 + PCl_5 \rightarrow \underset{(I)}{(PhO)_2P(O)N{=}PCl_3}$$

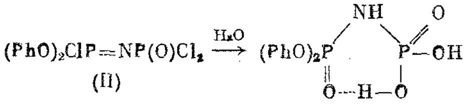
The structure of (I) was in agreement with the elemental analysis data and the chemical properties (reaction with water, aniline, and formic acids). Later it was established [2] that the amides of phosphoric, phosphonic, and phosphinic acids react with PCl_5 to give isomeric products:

$$RR'P(O)N{=}PCl_3 \overset{PCl_5}{\leftarrow\!\times\!-} RR'P(O)NH_2 \rightarrow RR'ClP = NP(O)Cl_2$$
$$R,\ R' = Alk,\ Ph.$$

PCl_5 reacts in a similar manner with the amides of the alkyl and phenyl esters of methyl- and chloromethylphosphonic acids [3, 4] (cf. [5]), and only the amide of bis(trichloromethyl)phosphinic acid reacts with PCl_5 to give give the unisomerized product [6]. The reasons for this difference were discussed in detail in [3].

The presence of two phenoxy groups in the amide of phosphoric acid, which have lower acceptor properties than trichloromethyl groups, also permits postulating the possible formation of the isomeric product, namely diphenyl(dichlorophosphorylimido)chlorophosphate (II), in the reaction with PCl_5.

This postulation was verified in the present paper and the structure of the reaction product of diphenyl amidophosphate with PCl_5 was established. Recently, we found [7] that, using a 1:2 ratio of the reactants, the pentachloride $Cl_3P = NP(O)Cl_2$ reacts with phenol to give imidophosphate (II), whose structure was rigorously proved. The hydrolysis of this imidophosphate (II) gives a crystalline compound, which on the basis of the elemental analysis, ^{31}P NMR, and IR spectral data was assigned the structure of diphosphorylimide (III):



(II) (III)

Imide (III) can also be formed from imidophosphate (I). Consequently, to ascertain the structure of the product obtained in [1], we repeated the syntheses described in this paper. It proved that the obtained compound is identical with imidophosphate (II), which was synthesized from the pentachloride and phenol (Table 1). Identical products are also formed when the compound, described in [1], and imidophosphate (II) are hydrolyzed. To conclusively prove the structure of the compound, described in [1], we employed its reaction with Me_2NH. If this compound has the structure of (I), then the formation of hexamethyltriamido(diphenoxyphosphorylimido)phosphate (IV) could be expected; if its structure corresponds to (II), then reaction with Me_2NH gives diphenyldimethylamido(tetramethyldiamidoimido)phosphate (V). Imidophosphates (IV) and (V) were synthesized by counter synthesis, as is shown below:

$$(Me_2N)_3P + N_3P(O)(OPh)_2 \rightarrow (Me_2N)_3P = \underset{(IV)}{NP(O)(OPh)_2}$$
$$(Me_2N)(PhO)_2P + N_3P(O)(NMe_2)_2 \rightarrow (Me_2N)(PhO)_2P = \underset{(V)}{NP(O)(NMe_2)_2}$$

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1137-1139, May, 1981. Original article submitted July 31, 1980.

0568-5230/81/3005-0897$07.50

TABLE 1. Characteristics of Compounds (II)-(V)

Compound	Yield, %	bp, °C $3 \cdot 10^{-3}$ mm Hg	n_D^{20}	d_4^{20}	Found/Calculated, %			Empirical formula	Infrared spectrum (ν, cm^{-1})		PMR spectrum (δ, ppm)		^{31}P NMR spectrum (δ, ppm)		J_{PNP}, Hz
					Cl	P	N		P=N	P=O	Me$_2$N (P=N)	Me$_2$N (P=O)	P′	P″	
$(PhO)_2ClP'=NP''(O)Cl_2$ (II)	72 [a]	128–129	1,5621	1,4437	27,7 27,7	16,1 16,1		$C_{12}H_{10}Cl_3NP_2O$	1360	1270	–	–	–11,8	–12,3	46,4
$(PhO)_2P'(O)NHP''(O)(OH)_2$ (III)	83 [b]	mp 172–173	–	–	–	19,1 18,8	–	$C_{12}H_{13}NO_6P_2$	–	–	–	–	–9,3	–0,5	9,8
$(Me_2N)_3P'=NP''(O)(OPh)_2$ (IV)	75	162–164	1,5463	1,1964		14.8 15,1		$C_{18}H_{28}N_4O_3P_2$	1300	1255	2,52	–	24,1	–11,4	34,1
$(PhO)_2(Me_2N)P'==NP''(O)(NMe_2)_2$ (V)	67 [c]	140–144	1,5417	1,1831		14,9 15,1	14,0 13,7	the same	1330	1200	2,93	2,41	–6,9	9,4	51,2

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[a] Reaction product of diphenyl amidophosphate with PCl_5; for the reaction product of $Cl_3P = NPOCl_2$ with phenol [7]: n_D^{20} 1.5632, d_4^{20} 1.4466. ^{31}P NMR (δ, ppm): –11.8 (P′), –12.6 (P″), J_{PNP} = 45.5 Hz.

[b] Hydrolysis product of $(PhO)_2ClP = NPOCl_2$ (II). Found: C 43.5, H 3.7%. Calculated: C 43.7, H 4.0%. Data from [1]: mp 172-173°.

[c] Reaction product of compound, obtained as described in [1], with dimethylamine. For the reaction product of $(PhO)_2PNMe_2$ with $(Me_2N)_2P(O)N_3$ [7]: bp 140-142° (0.001 mm), n_D^{20} 1.5404, d_4^{20} 1.1816; ^{31}P NMR (δ, ppm): –7.1 (P′), 9.4 (P″), J_{PNP} = 51.5 Hz.

It proved that the compound, obtained as described in [1], when reacted with Me_2NH gives a product that is identical with the imidophosphate (V) obtained by counter synthesis (see Table 1).

From the obtained data it follows that the reaction of diphenyl amidophosphate with PCl_5 gives (II), and not (I).

EXPERIMENTAL

The IR spectra were recorded on a UR-20 instrument as a liquid film, the PMR spectra were recorded on a Perkin–Elmer R-12 instrument in CCl_4 solution and using TMS as the internal standard, and the ^{31}P NMR spectra were recorded on a Bruker HX-90 instrument with decoupling from the protons (the chemical shifts downfield from the standard were considered to be positive).

The compound, described in [1], and its hydrolysis product, namely imide (III), were obtained as described in the paper; diphenyl(dichlorophosphorylimido)chlorophosphate (II) and diphenyldimethylamido(tetramethyldiamidoimido)phosphate (V) were obtained as described in [7].

Diphenoxyphosphoryl(dihydroxyphosphoryl)imide (III). To 4.2 g of (II) was added 7.0 g of water and the mixture was let stand for 2 days at ~20°. The obtained crystalline compound was separated and then reprecipitated from dioxane solution with ether to give 3.4 g of (III).

Hexamethyltriamido(diphenoxyphosphorylimido)phosphate (IV). To 3.4 g of hexamethyltriamidophosphite in 5.0 ml of benzene was slowly added a solution of 4.8 g of diphenylazidophosphate in 2.0 ml of benzene. The mixture was kept at 80-85° until the absorption band of the azido group disappeared in the IR spectrum. Then the volatiles were distilled off and the residue was distilled to give 5.3 g of (IV).

Reaction of Compound, Described in [1], with Dimethylamine. To a stirred solution of 5.2 g of the indicated compound in 80 ml of abs. ether at 0–5° was added a solution of 5.6 g of dimethylamine in 20 ml of ether. The mixture was kept for 3 h at ~20° and then filtered. The volatiles were distilled off and the residue was distilled to give 3.7 g of (V).

EXPERIMENTAL

Contrary to the literature data, the reaction of diphenyl amidophosphate with PCl_5 gives diphenyl(dichlorophosphorylimido)chlorophosphate, and not (diphenoxyphosphorylimido)trichlorophosphate.

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